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## **Tl<sub>2</sub>Te and its relationship with Tl<sub>5</sub>Te<sub>3</sub>**

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The crystal structure of Tl<sub>2</sub>Te, dithallium telluride, has been determined by single-crystal X-ray diffraction. The analysis of the structure shows that this compound is the first known representative of a new crystal structure type. The structural relationship with the related Tl<sub>5</sub>Te<sub>3</sub> phase is discussed.

## Comment

Although the existence of Tl<sub>2</sub>Te has been reported by many authors (Hahn & Klinger, 1949; Rabenau *et al.*, 1960; Vasilev *et al.*, 1968; Asadov *et al.*, 1977; Chami *et al.*, 1983), its crystal structure has remained undetermined and its existence has even been questioned (Chikashige, 1912; Klemm & Vogel, 1934; Oh & Lee, 1993). Using differential scanning calorimetry and powder X-ray diffraction, a study of the Tl–Te phase diagram was undertaken by Record *et al.* (1997), in which the existence of this phase was unambiguously confirmed. We report here on the crystal structure of Tl<sub>2</sub>Te and its relation to Tl<sub>5</sub>Te<sub>3</sub>.

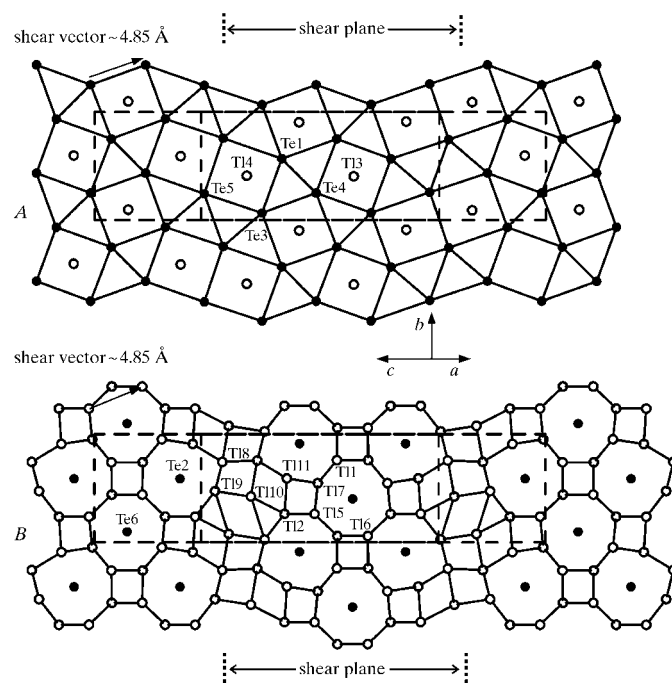
The crystal structure of Tl<sub>2</sub>Te can be described as two alternating types of (*h*0*h*) layers, similar to those found in the structure of Tl<sub>5</sub>Te<sub>3</sub> [Fig. 1 in Schewe *et al.* (1989)]. Layer type *A* is a quasi-planar layer at  $x + z = 0, \frac{1}{2}, 1$  and  $\frac{3}{2}$ . Layer type *B* is a puckered layer (thickness 2.5 Å) at  $x + z = \frac{1}{4}, \frac{3}{4}, \frac{5}{4}$  and  $\frac{7}{4}$ . Layer *A* (Fig. 1) corresponds to the layer found at  $z = 0$  and  $\frac{1}{2}$  in Tl<sub>5</sub>Te<sub>3</sub>, while layer *B* (Fig. 1) corresponds to the layer found at  $z = \frac{1}{4}$  and  $\frac{3}{4}$  in Tl<sub>5</sub>Te<sub>3</sub>.

Layer *A* is described in Tl<sub>5</sub>Te<sub>3</sub> as being formed from a 3<sup>2</sup>434 net of Te atoms centred by a 4<sup>4</sup> net of Tl atoms. Bands of width ~18.3 Å containing basic motifs of this net are formed from atoms Tl3, Tl4, Te1, Te3, Te4 and Te5 in the structure of Tl<sub>2</sub>Te. These bands are oriented along the *b* axis and are repeated twice in the [10 $\bar{1}$ ] direction of the cell of Tl<sub>2</sub>Te. Neighbouring bands are mutually shifted from the ideal infinite nets found in Tl<sub>5</sub>Te<sub>3</sub> by a vector lying in the (*h*0*h*) plane having a length of ~4.85 Å (Fig. 1). The composition of layer *A* is identical in Tl<sub>2</sub>Te (Tl<sub>8</sub>Te<sub>16</sub>) and in Tl<sub>5</sub>Te<sub>3</sub> (Tl<sub>4</sub>Te<sub>8</sub>).

Layer *B* is described in Tl<sub>5</sub>Te<sub>3</sub> as being formed from a 48<sup>2</sup> net of Tl atoms centred by a 4<sup>4</sup> net of Te atoms. Bands of width ~14.7 Å containing basic motifs of this net are formed from atoms Tl1, Tl2, Tl5, Tl6, Tl7, Tl8, Tl9, Tl10, Tl11, Te2 and Te6 in the structure of Tl<sub>2</sub>Te. The bands are also oriented along the *b* axis and are repeated twice in the [10 $\bar{1}$ ] direction of the cell of Tl<sub>2</sub>Te. Neighbouring bands are again mutually shifted by the same vector as in layer *A*, and are separated by atomic chains containing only Tl atoms. The composition of layer *B* in Tl<sub>2</sub>Te is Tl<sub>36</sub>Te<sub>6</sub>, compared with Tl<sub>16</sub>Te<sub>4</sub> in Tl<sub>5</sub>Te<sub>3</sub>. The overall composition changes from Tl<sub>5</sub>Te<sub>3</sub> to Tl<sub>2</sub>Te.

The shears in layers *A* and *B* occur so that they form (002) shear planes. The stacking of layers *A* and *B* in the structure of Tl<sub>2</sub>Te, and the relation between the elementary cells of Tl<sub>2</sub>Te and Tl<sub>5</sub>Te<sub>3</sub>, are given in Fig. 2.

The structure of Tl<sub>5</sub>Te<sub>3</sub> has also been described as containing infinite straight Te–Tl–Te chains, with Tl–Te distances of 3.15 Å, and quasi-molecular Tl<sub>2</sub>Te groups, with Tl–Te distances of 3.16 Å. These chains propagate along the direction perpendicular to layers *A* and *B*. They can also be identified in the structure of Tl<sub>2</sub>Te. However, they are finite (Tl4–Te2–Tl3–Te6–Tl3–Te2–Tl4), because of the shears in the *A* and *B* layers, and distorted (Tl–Te distances between 3.14 and 3.34 Å). The Tl<sub>2</sub>Te groups can also be found in the structure of Tl<sub>2</sub>Te. However, the Tl–Te distance in the group varies between 3.15 and 3.30 Å.

**Figure 1**

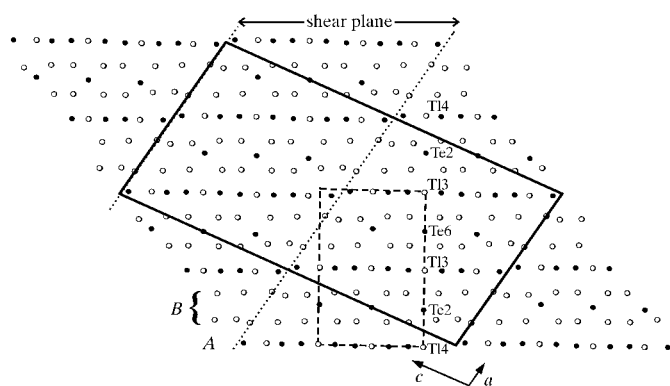
The structure of Tl<sub>2</sub>Te viewed in the direction ~[301]. Two basic units, the planar layer *A* and the puckered layer *B*, are shown. Open circles indicate Tl atoms and filled circles indicate Te atoms. Only the Te net in layer *A* and the Tl net in layer *B* are shown. The position of the shear plane is marked by a dashed line in each unit. The shear vector between two Tl<sub>5</sub>Te<sub>3</sub>-like regions is also shown.

The coordination of Tl and Te atoms in the structure of  $\text{Tl}_2\text{Te}$  is derived from that in the structure of  $\text{Tl}_5\text{Te}_3$ . The Tl atoms lying in the *A* layer of the  $\text{Tl}_5\text{Te}_3$  structure are coordinated by a  $\text{Te}_{4+2}$  octahedron in the first sphere and by a  $\text{Tl}_8$  cube in the second sphere. This coordination is nearly preserved in the  $\text{Tl}_2\text{Te}$  structure for atom Tl3, with slightly longer Tl–Te distances (3.30–3.42 Å) in the  $\text{Te}_6$  octahedron and in the deformed  $\text{Tl}_8$  cube (Tl–Tl distances of 3.82–4.09 Å). For atom Tl4, lying on the shear plane, the coordination is  $\text{Te}_5$  (Tl–Te distances of 3.15–3.85 Å) and  $\text{Tl}_8$  (Tl–Tl distances of 3.32–3.99 Å).

The Tl atoms in the *B* layer of the  $\text{Tl}_2\text{Te}$  structure are coordinated in the first sphere in a way similar to the Tl atoms in the *B* layer of the  $\text{Tl}_5\text{Te}_3$  structure (distorted trigonal prism,  $\text{Te}_3\text{Tl}_3$ ), with Tl–Te distances 3.15–3.54 Å and Tl–Tl distances of 3.35–3.73 Å. The Tl9–Tl4 (3.32 Å), Tl9–Tl8 (3.37 Å) and Tl10–Tl11 (3.35 Å) distances, found near the shear plane, correspond well with the distance in metallic Tl (3.35 Å).

The Te atoms in the *A* layer of the  $\text{Tl}_2\text{Te}$  structure lying outside the shear plane (atoms Te1, Te3 and Te4) are coordinated in a similar way to the Te atoms in the *A* layer of the  $\text{Tl}_5\text{Te}_3$  structure (distorted bicapped trigonal prism,  $\text{Tl}_8$ ), with Te–Tl distances of 3.15–3.58 Å. Atom Te5, lying on the shear plane, is coordinated by a distorted trigonal prism,  $\text{Tl}_6$ , with Te–Tl distances of 3.30–3.43 Å. Atom Te6, lying in the *B* layer outside the shear plane, is coordinated as in the  $\text{Tl}_5\text{Te}_3$  structure, by a compressed bicapped tetragonal antiprism, with Te–Tl distances of 3.31–3.69 Å. Atom Te2, lying in the *B* layer close to the shear plane, is coordinated by a distorted tetragonal antiprism, with Te–Tl distances of 3.14–3.68 Å.

The crystal structure of  $\text{Tl}_2\text{Te}$  can be rationalized as being composed from regions with the structure of  $\text{Tl}_5\text{Te}_3$  and regions which contain only Tl atoms, some of them showing Tl–Tl distances corresponding to metallic Tl. This description is further supported by the decomposition of  $\text{Tl}_2\text{Te}$  into  $\text{Tl}_5\text{Te}_3$  and Tl on heating (Rabenau *et al.*, 1960; Vasilev *et al.*, 1968; Schewe *et al.*, 1989). We have observed such phase transformation on a bulk sample of  $\text{Tl}_2\text{Te}$ , by powder diffraction and



**Figure 2**  
The stacking of layers *A* and *B* in the structure of  $\text{Tl}_2\text{Te}$  viewed in the [010] direction. The  $\text{Tl}_2\text{Te}$  cell is shown by a solid line and the  $\text{Tl}_5\text{Te}_3$  cell by a dashed line. Open circles indicate Tl atoms and filled circles indicate Te atoms. The position of the shear plane is marked by a dashed line.

Rietveld refinement. After several days of the sample being exposed to air, it had nearly completely transformed to the  $\text{Tl}_5\text{Te}_3$  phase and thallium oxides. According to the analysis of the  $\text{Tl}_5\text{Te}_3$  structure by Schewe *et al.* (1989), the bond analysis of the Tl–Te system by Bhan & Schubert (1970), the chemical composition and the absence of Te–Te bonds in the structure of  $\text{Tl}_2\text{Te}$ , we expect that Tl has the oxidation state  $\text{Tl}^{1+}$  in  $\text{Tl}_2\text{Te}$ , and that the compound is metallic.

The structures of  $\text{Tl}_5\text{Te}_3$  and  $\text{Tl}_2\text{Te}$  are closely related and, indeed, the crystal studied here was intergrown from two domains, one with the  $\text{Tl}_2\text{Te}$  structure and the other having a cubic face-centred lattice, with  $a_c = 12.70$  Å. The diffraction pattern of the  $\text{Tl}_5\text{Te}_3$  structure shows a strong face-centred cubic pseudosymmetry, with  $a_c = 12.60$  Å, following the relationship  $a_t = \frac{1}{2}(-a_c + c_c) = 8.98$  Å,  $b_t = \frac{1}{2}(a_c + c_c) = 8.98$  Å and  $c_t = b_c = 12.60$  Å. Some authors have even reported a diffraction pattern corresponding to a cubic lattice, with a lattice parameter of approximately 12.60 Å (Man *et al.*, 1971; Anseau, 1973).

The  $\text{Tl}_5\text{Te}_3$  phase shows a small range of homogeneity of several atomic% Tl. Whether, within this homogeneity range, the structure can change from pseudocubic to true cubic, and whether our second domain corresponds to that cubic structure or to the tetragonal  $\text{Tl}_5\text{Te}_3$  structure, cannot be answered here, because of the small size of the second domain. The monoclinic cell of the  $\text{Tl}_2\text{Te}$  structure can also be related to the cubic cell with  $a_c = 12.70$  Å. However, the deviation from the cubic lattice is much greater than in the case of the tetragonal  $\text{Tl}_5\text{Te}_3$  cell. We have observed the following relationship between the lattices of the first domain (monoclinic) and the second domain (cubic) with  $a_c = 12.70$  Å:  $a_m \sim \frac{1}{2}(-a_c + 2b_c - c_c) = 15.55$  Å,  $b_m = \frac{1}{2}(-a_c + c_c) = 8.98$  Å and  $c_m \sim 2a_c + b_c + 2c_c = 28.40$  Å.

## Experimental

The analytical sample was composed of weighed samples of pure thallium (Fluka, 4 N, 0.995 g) and pure tellurium (Fluka, 5 N, 0.299 g). Non-soluble impurities were removed from the tellurium by filtration under purified argon on silica wool. The thin oxide layer on the surface of the pure thallium pellets was removed using sulfuric acid baths (0.1 N) followed by rinsing in acetone. The alloy was then formed by direct fusion of the pure elements in a silica tube sealed under vacuum ( $10^{-1}$  Pa). The composition of the alloy ( $x_{\text{Te}} = 0.325$ ) was chosen to ensure that the  $\text{Tl}_2\text{Te}$  phase ( $x_{\text{Te}} = 0.333$ ) was obtained even in the event of evaporation or oxidation of the thallium. Subsequent annealing was performed for 160 h at 553 K. For X-ray data collection, the crystal was covered with a protective layer of perfluoropolyalkyl ether (ABCR GmbH & Co.) to prevent its oxidation and decomposition.

### Crystal data

$\text{Tl}_2\text{Te}$   
 $M_r = 536.37$   
Monoclinic,  $C2/c$   
 $a = 15.6621$  (9) Å  
 $b = 8.9873$  (4) Å  
 $c = 31.196$  (2) Å  
 $\beta = 100.761$  (7)°  
 $V = 4313.9$  (4) Å<sup>3</sup>  
 $Z = 44$

$D_x = 9.084$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 2000 reflections  
 $\theta = 3$ –25°  
 $\mu = 89.10$  mm<sup>-1</sup>  
 $T = 293$  K  
Parallelepiped, metallic dark grey  
0.15 × 0.03 × 0.03 mm

**Table 1**  
Selected interatomic distances (Å).

Tl1—Te3	3.266 (3)	Tl5—Te2 <sup>xi</sup>	3.560 (4)
Tl1—Te4	3.356 (4)	Tl5—Tl6	3.592 (3)
Tl1—Te1	3.457 (4)	Tl6—Te4	3.175 (4)
Tl1—Tl7 <sup>i</sup>	3.508 (3)	Tl6—Te4 <sup>xii</sup>	3.453 (4)
Tl1—Tl1 <sup>ii</sup>	3.586 (2)	Tl6—Te1 <sup>xiii</sup>	3.462 (3)
Tl1—Tl6 <sup>iii</sup>	3.631 (3)	Tl6—Tl6 <sup>xiii</sup>	3.514 (3)
Tl2—Te4	3.241 (3)	Tl7—Te4 <sup>viii</sup>	3.151 (3)
Tl2—Te3	3.272 (4)	Tl7—Te4	3.297 (4)
Tl2—Te1	3.344 (4)	Tl7—Te6 <sup>xi</sup>	3.396 (3)
Tl2—Tl9 <sup>iv</sup>	3.460 (3)	Tl7—Tl11 <sup>v</sup>	3.421 (2)
Tl2—Tl5	3.514 (3)	Tl8—Te1	3.182 (3)
Tl2—Tl11 <sup>v</sup>	3.692 (3)	Tl8—Te3 <sup>vii</sup>	3.338 (4)
Tl3—Te6	3.3016 (17)	Tl8—Tl9 <sup>v</sup>	3.372 (3)
Tl3—Te2 <sup>vi</sup>	3.329 (3)	Tl8—Te5 <sup>xiv</sup>	3.407 (4)
Tl3—Te1	3.354 (4)	Tl8—Tl11 <sup>v</sup>	3.693 (3)
Tl3—Te3 <sup>vii</sup>	3.403 (3)	Tl8—Tl10 <sup>vii</sup>	3.739 (3)
Tl3—Te4 <sup>vii</sup>	3.417 (4)	Tl9—Te2 <sup>xiv</sup>	3.175 (3)
Tl3—Te4 <sup>iii</sup>	3.422 (3)	Tl9—Te5 <sup>xiv</sup>	3.283 (4)
Tl4—Te2 <sup>ix</sup>	3.154 (3)	Tl9—Te5	3.300 (4)
Tl4—Te1 <sup>ix</sup>	3.234 (4)	Tl10—Te3	3.229 (3)
Tl4—Tl9 <sup>ix</sup>	3.314 (2)	Tl10—Te5	3.293 (4)
Tl4—Te3 <sup>ix</sup>	3.363 (4)	Tl10—Tl11 <sup>xv</sup>	3.335 (3)
Tl4—Te5 <sup>x</sup>	3.676 (4)	Tl10—Te5 <sup>xvi</sup>	3.371 (4)
Tl4—Te5 <sup>ix</sup>	3.846 (4)	Tl11—Te2 <sup>xiv</sup>	3.170 (4)
Tl5—Te1 <sup>xi</sup>	3.186 (4)	Tl11—Te3 <sup>xiv</sup>	3.256 (4)
Tl5—Te3 <sup>vi</sup>	3.397 (4)	Tl11—Te5 <sup>xiv</sup>	3.433 (3)
Tl5—Tl7	3.560 (3)		

Symmetry codes: (i)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (ii)  $1 - x, y, \frac{3}{2} - z$ ; (iii)  $\frac{1}{2} + x, y - \frac{1}{2}, z$ ; (iv)  $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (vi)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (vii)  $x, y - 1, z$ ; (viii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (ix)  $x, 1 - y, z - \frac{1}{2}$ ; (x)  $1 - x, y, \frac{1}{2} - z$ ; (xi)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (xii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (xiii)  $-x, y, \frac{3}{2} - z$ ; (xiv)  $1 - x, 1 - y, 1 - z$ ; (xv)  $x, 1 + y, z$ ; (xvi)  $1 - x, 2 - y, 1 - z$ .

**Data collection**

Stoe IPDS diffractometer  
 $\varphi$  oscillation scans  
 Absorption correction: analytical  
 (*X-RED*; Stoe & Cie, 1999)  
 $T_{\min} = 0.019$ ,  $T_{\max} = 0.127$   
 12 622 measured reflections  
 3865 independent reflections  
 1989 reflections with  $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.153$   
 $\theta_{\text{max}} = 25.9^\circ$   
 $h = -19 \rightarrow 19$   
 $k = -11 \rightarrow 10$   
 $l = -38 \rightarrow 38$   
 200 standard reflections  
 frequency: 10 min  
 intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.107$   
 $wR(F^2) = 0.180$   
 $S = 2.37$   
 1982 reflections  
 150 parameters  
 Weighting scheme based on  
 measured s.u.'s

$(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 8.97 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -8.32 \text{ e } \text{Å}^{-3}$   
 Extinction correction: B–C type 1  
 Gaussian isotropic (Becker &  
 Coppens, 1974)  
 Extinction coefficient: 0.005

Two non-coherent domains were identified in the crystal. The first domain had the  $\text{Tl}_2\text{Te}$  structure and the second had a cubic face-

centred lattice. The reflections of both domains were separated in the process of integrating the images. From 15 502 measured reflections of the first domain, 2880 reflections were rejected because of overlap with reflections of the second domain and mean  $F^2/\sigma(F^2) = 4.6$ . In the second domain, 7317 reflections were measured and mean  $F^2/\sigma(F^2) = 1.9$ . The  $R$  factors show no systematic deviation of different reflection groups from the mean, whether in dependence on  $hkl$ ,  $F_{\text{obs}}$  or  $\sin(\theta)/\lambda$ . No warnings of twinning were observed. The value of  $R_{\text{int}}$  and the difference Fourier maps were calculated using 1989 observed reflections. The highest peaks in the difference Fourier map are within 1 Å of the atom sites.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS Software*; data reduction: *ADDRESS* and *SORTRF* in *Xtal3.7* (Hall *et al.*, 2000), and *TWIN* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *LSLS* in *Xtal3.7*; molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal3.7*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1351). Services for accessing these data are described at the back of the journal.

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